

Stable Isotopes as Tracers of Sources and Processes Related to Nitrate Distributions in Domestic Supply Wells in the San Joaquin Valley, California

Task Report 4

Project

“Long Term Risk of Groundwater and Drinking Water Degradation from Dairies and Other Nonpoint Sources in the San Joaquin Valley”

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Abstract

The dual stable isotopic composition of nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}-\text{NO}_3$) can provide information regarding nitrogen sources and processes influencing the distribution of dissolved nitrate concentrations within the environment. Nitrate derived from chemical fertilizers generally has a much lower range of $\delta^{15}\text{N}-\text{NO}_3$ values in comparison to nitrate derived from animal or human waste, although biogeochemical processes can also shift the nitrate isotope values. $\delta^{15}\text{N}-\text{NO}_3$ values greater than +10‰ typically indicate either a significant contribution of human or animal waste-derived nitrate, and/or significant denitrification. Processes such as denitrification and nitrification will result in distinct relationships between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}-\text{NO}_3$, nitrate concentrations, and water isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}-\text{H}_2\text{O}$), and these relationships can often be used to distinguish between isotopic source signatures, and isotopic values primarily controlled by in-situ processes. In this study, nitrate and water isotopic compositions were measured from 200 domestic drinking water wells located in the San Joaquin Valley in order to better understand the nitrogen sources and processes influencing nitrate concentrations within these wells. Wells were grouped into four major categories based on geographic location and proximity to dairy-related land use (waste lagoons or dairy corrals). Half of the wells ($n=100$) were located in Stanislaus and Merced Counties (Stan/Mer) and the other half were located in Tulare and Kings Counties (Tul/Kings). Within each geographic region, wells were grouped into either dairy or non-dairy categories, with wells located within 2.4 km of a dairy corral and lagoon designated as dairy.

With the exception of two Tul/Kings non-dairy wells, all $\delta^{15}\text{N}-\text{NO}_3$ values above +10‰ were measured in dairy region wells. Nitrate isotope values in domestic wells in dairy regions showed a very similar trend to the isotope values measured in the dairy monitoring wells (near the top of the water table), although the $\delta^{15}\text{N}-\text{NO}_3$ values in the dairy monitoring wells extended into a much higher range. Domestic wells had lower median $\delta^{15}\text{N}-\text{NO}_3$ values than the dairy monitoring wells, suggesting less contribution of manure-derived nitrate in comparison to the first-encountered groundwater sampled in the Stan/Mer dairy monitoring wells. In Stan/Mer, the dairy domestic wells had significantly higher mean and median $\delta^{15}\text{N}-\text{NO}_3$ values in comparison to the non-dairy domestic wells, and 35% of the dairy wells had $\delta^{15}\text{N}-\text{NO}_3$ values above +10‰, suggesting significant contributions of waste-derived nitrate. None of the Stan/Mer non-dairy wells had $\delta^{15}\text{N}-\text{NO}_3$ values $\geq +10$ ‰. In Tul/Kings, mean $\delta^{15}\text{N}-\text{NO}_3$ values were significantly higher in dairy wells in comparison to the non-dairy wells, although the median $\delta^{15}\text{N}-\text{NO}_3$ values were very similar (+6.0‰ and +5.8‰, respectively). In Tul/Kings, 19% of the dairy wells with sufficient nitrate for isotopic analysis had $\delta^{15}\text{N}-\text{NO}_3$ values above +10‰, while only 2 (4%) of the non-dairy wells were above +10‰. In the Stan/Mer and Tul/Kings dairy well groups, $\delta^{15}\text{N}-\text{NO}_3$ was significantly negatively correlated to distance from a dairy corral or waste lagoon (Spearman's $\rho = -0.52$ and -0.55 , respectively, $p < 0.001$), consistent with higher manure-derived $\delta^{15}\text{N}-\text{NO}_3$ values occurring within closer proximity to dairies. In both non-dairy groups, $\delta^{15}\text{N}-\text{NO}_3$ was not significantly correlated to distance from dairy. For the entire well group, $\delta^{15}\text{N}-\text{NO}_3$ was not significantly correlated to

NO₃ concentration, indicating that manure-derived nitrate is only one of several controlling factors for nitrate concentrations in these wells.

Within the four well groups, distinct relationships were seen between nitrate isotopic composition, nitrate concentrations, and water isotopic composition, indicating that different sources and processes exerted different levels of influence across the well groups. In both the Stan/Mer and Tul/Kings dairy groups, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3$ showed a linear relationship, consistent with either denitrification or with mixing of manure-derived nitrate, as defined by the nitrate isotope values measured in the shallow dairy monitoring wells in the Stan/Mer region. Nitrate concentrations and dissolved oxygen patterns were not consistent with in-situ denitrification, suggesting that high $\delta^{15}\text{N}\text{-NO}_3$ values in the domestic wells were controlled by a combination of manure isotopic source signature and partial denitrification prior to reaching groundwater. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3$ did not have a linear relationship in either of the non-dairy well groups. In the Tul/Kings non-dairy wells, $\delta^{18}\text{O}\text{-NO}_3$ was significantly correlated to $\delta^{18}\text{O}\text{-H}_2\text{O}$ (Spearman's rho = 0.58, p < 0.001), suggesting the influence of in-situ nitrification in which oxygen from the surrounding water and dissolved oxygen are incorporated into the nitrate molecule when it is formed from another nitrogen species. The oxygen isotope data for both groups of non-dairy wells was also consistent with contributions of high $\delta^{18}\text{O}$ nitrate derived from synthetic nitrate fertilizer, and the possible influence of nitrification cannot be distinguished from that of synthetic nitrate fertilizer at this time.

Further information (publications, related reports, multi-media materials) is available at <http://groundwater.ucdavis.edu>.

1. Introduction

Nitrate contamination of groundwater is a major concern in the Central Valley, California, and concentrations above the EPA drinking water limit of 10 mg/L NO₃-N have been found in many domestic drinking water wells throughout the Central Valley. The San Joaquin Valley is located within the Central Valley, and is dominated by agricultural land use including a wide variety of crop types as well as concentrated animal feeding operations (CAFOs) primarily consisting of dairies. There are many potential sources of nitrate contamination to drinking water wells within the San Joaquin Valley including synthetic fertilizers, manure, and septic systems. Due to the complex mix of land uses throughout the San Joaquin Valley, it can be very difficult to determine either the dominant source of nitrate to an individual well, or to understand the mixture of various nitrogen sources and biogeochemical processes controlling nitrate concentrations in the drinking water.

Stable isotope analysis can often provide information about the sources and processes affecting the concentrations and/or distributions of a given substance which cannot be determined from concentration analysis alone. Many elements have more than one stable isotope, meaning that the atoms of the element have the same number of protons and electrons, but a different number of neutrons, and therefore a different atomic weight. For example, approximately 99.6% of all nitrogen atoms on Earth have 14 protons and 14 neutrons (referred to as ¹⁴N), while approximately 0.37% of the nitrogen atoms have 14 protons and 15 neutrons (¹⁵N). Stable isotopes are measured and reported as a ratio of the heavy to the light isotope relative to an international standard, using delta units (δ) and “per mil” notation, denoted with the symbol “‰”. Isotope values are calculated using the following equation:

$$\delta_{\text{sample}} (\text{‰}) = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000$$

where R is the ratio of the lighter isotope to the heavier isotope in either the sample or the standard. Various physical and biological processes can alter the distributions of stable isotopes within a given pool of the element, resulting in distinct isotopic patterns which can be linked to certain dominant sources and/or processes.

In this study we focused on the use of nitrate (^δ¹⁵N and ^δ¹⁸O-NO₃) and water (^δ¹⁸O and ^δ²H - H₂O) stable isotopes in combination with concentration measurements, physio-chemical parameters, and land-use patterns to better understand the sources and processes influencing nitrate concentrations in a set of 200 domestic drinking water wells in the San Joaquin Valley. ^δ¹⁵N and ^δ¹⁸O of nitrate each provide different types of information about dominant nitrate sources, and critical processes related to nitrate distribution in groundwater such as nitrification, denitrification, and physical mixing will result in different relationships between the two isotopes. Water isotopes reflect the precipitation source of the water (^δ¹⁸O and ^δ²H-H₂O in precipitation are controlled by temperature,

elevation, and continental effects), mixing between different water sources, and evaporation (Epstein and Mayeda, 1953; Freidman et al., 1964).

Major sources of nitrate to surface and groundwater often have distinct nitrate isotope compositions, which can be used to identify and separate potential sources of nitrate within a given set of water samples (**Figure 1**; reviewed in Kendall et al., 2007, Xue et al., 2009). However, other processes such as physical mixing between two or more nitrate sources, and biogeochemical processes including denitrification, algal and bacterial nitrate uptake, and nitrification can alter the original isotopic signature, either complicating or completely obscuring interpretation of nitrate source signatures. We therefore use multiple lines of evidence including physiochemical parameters like dissolved oxygen content (suboxic to anoxic conditions are required for denitrification) and chemical composition in order to determine whether original source signatures are the dominant control on the measured nitrate isotope values within a sample set, or whether specific processes are controlling nitrate concentration and isotope composition.

If mixing and biogeochemical process have not significantly altered the original isotope composition, then $\delta^{15}\text{N-NO}_3$ combined with nitrate concentration can frequently be used to distinguish between animal/human waste, natural soil-derived nitrate, and nitrate from chemical fertilizers. The distinct isotope values occur because chemical fertilizers typically have low $\delta^{15}\text{N}$ values for all forms of nitrogen used in the fertilizer, and nitrifying bacteria will preferentially convert the isotopically lighter nitrogen into nitrate first, resulting in low $\delta^{15}\text{N-NO}_3$ values (Flipse and Bonner, 1985; Wassenaar, 1995, Kendall 1998). If all of the fertilizer nitrogen is converted to nitrate, then the new nitrate will be isotopically identical to the original fertilizer nitrate, which also has a low $\delta^{15}\text{N}$ value. Synthetic fertilizer in the form of nitrate typically has low $\delta^{15}\text{N-NO}_3$ values similar to other synthetic fertilizer forms, but has distinct elevated $\delta^{18}\text{O-NO}_3$ values (approximately +17 to +25‰) because the oxygen in the synthetic nitrate is derived from atmospheric O_2 with a $\delta^{18}\text{O}$ value of +23.5‰ (Amberger and Schmidt, 1987, Xue et al., 2009). In contrast, nitrate from human and animal waste typically has much higher $\delta^{15}\text{N-NO}_3$ values in comparison to fertilizer-derived nitrate. This is because physical processing of animal and human waste allows for significant amounts of ammonium volatilization prior to eventual conversion of the ammonium to nitrate. Ammonium volatilization is a physical process with very high isotopic fractionation, in which NH_4 converts to NH_3 gas, with the lighter nitrogen preferentially entering the gas form and leaving the system. The volatilization leaves the remaining NH_4 highly enriched in $\delta^{15}\text{N}$, and this signal is passed on to the nitrate as it is formed (Aravena et al 1993; Wassenaar 1995; Fogg et al 1998; Sebilo et al 2006).

The major processes expected to influence nitrate distribution in groundwater are denitrification, nitrification, and physical mixing of waters with different nitrate isotopic compositions. Denitrification is the microbial processes by which nitrate is reduced to a gas (N_2 , N_2O , or NO). Denitrification typically requires low oxygen levels and a source of organic matter, although it may occur in anaerobic microsites within aerobic environments (Koba et al, 1997). Denitrification will preferentially remove the light isotopes of both N and O from the remaining NO_3 pool, resulting in a coupled increase in both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O-NO}_3$, concurrent with a decrease in the NO_3 concentration (Kendall et al.,

2007). A wide range of isotope enrichment factors for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ has been reported for denitrification, and a linear relationship between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ - NO_3 with a slope between 0.5 and 0.8 has been identified as an indicator of denitrification in aquatic systems (Aravena and Robertson, 1998; Xue et al., 2009). Nitrification, in which NH_4 is converted first to NO_2 , then to NO_3 , will initially result in new nitrate with a $\delta^{15}\text{N}$ - NO_3 value significantly lighter than the original N source, and will become isotopically identical to the original N source if complete nitrification occurs (Kendall 1998, Xue et al, 2009). The oxygen in the newly formed nitrate is derived from both the water and the dissolved oxygen in the water. It is estimated that two thirds of the oxygen comes from the water, and one third comes from dissolved oxygen (Anderson and Hooper, 1983). Therefore, the predicted oxygen isotopic composition of the new nitrate can be calculated using the following equation:

$$\delta^{18}\text{O}-\text{NO}_3 = 2/3 (\delta^{18}\text{O} -\text{H}_2\text{O}) + 1/3(\delta^{18}\text{O} -\text{O}_2)$$

It is typically assumed that the dissolved oxygen in the water retains the atmospheric isotope composition of +23.5‰, however, depletion of dissolved oxygen within the groundwater through various biogeochemical processes may result in isotopic enrichment (heavier isotope values) of the remaining dissolved oxygen (Kendall, 1998; Sebilo et al., 2006).

The goals of the stable isotope portion of the domestic well study were to 1) identify the ranges of nitrate isotopic compositions found in the domestic wells for comparison to other studies and potential future sampling of the same wells, 2) determine if and where $\delta^{15}\text{N}$ - NO_3 values indicated the contribution of manure-derived nitrate, 3) identify the dominant nitrogen sources and/or processes controlling nitrate concentrations in the Stan/Mer and Tul/Kings region as related to dairy and non-dairy land use, and 4) use water isotope compositions to identify potential sources of water to the wells, identify water impacted by evaporation, and identify areas where in-situ nitrification may be an important component of total nitrate concentrations.

2. Methods

2.1 Project Area and Sample Collection

See the Task Report “Identifying Sources of Groundwater Nitrate Contamination in a Large Alluvial Groundwater Basin with Highly Diversified Intensive Agricultural Production” for a detailed description of the study area, methods for selection of the sampled wells, and field sampling techniques. As described in that Task Report, domestic wells were given a designation of either “dairy” or “non-dairy” based on the proximity of the well to either a dairy corral or waste lagoon area. Wells with either a dairy corral or waste lagoon within a 1.5 mile (2.4 km) radius were designated “dairy” while wells with no waste lagoons or corrals within the 1.5 mile radius were designated “non-dairy”. Within the entire study, two main types of wells were sampled: domestic wells which were not installed as part of this study, and were designed for the purpose of extracting drinking water, and dedicated monitoring wells, many of which were installed specifically for this study, and were designed in order to collect samples near the top of the water table. In order to distinguish between these different types of wells within this chapter, the monitoring wells will always be referred to as “dairy monitoring wells” or “monitoring wells”, while the domestic wells will be referred to as “wells”, with the appropriate group designation (Stan/Mer wells, Tul/Kings wells, Stan/Mer dairy wells, Stan/Mer non-dairy wells, Tul/Kings dairy wells, Tul/Kings non-dairy wells).

Samples for nitrate isotope analysis were filtered in the field through a 0.45 micron filter into 60mL wide mouth screw-cap HDPE bottles, with a small amount of headspace to leave room for expansion during freezing. Nitrate isotope samples were stored in a cooler in the dark, and then frozen upon return to the laboratory. Samples were stored frozen and then thawed in a room temperature water bath prior to analysis. Water isotope samples were collected in 20mL plastic scintillation vials with polyseal cone caps in order to prevent evaporation, and stored at room temperature prior to analysis.

2.2 Nitrate Isotope Analysis

The Menlo Park U.S. Geological Survey Stable Isotope Laboratory uses the denitrifier method (Sigman et al., 2001, Casciotti et al., 2002) for simultaneous measurement of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of in which the nitrate is converted quantitatively to N_2O , which is then measured for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 in water samples. Briefly, splits of field-filtered sample water are thawed and aliquots were taken based upon measured nitrate concentrations. The aliquots are injected into sealed vials containing prepared colonies of *Pseudomonas aureofaciens* denitrifying bacteria and triptic soy broth media. The vials are allowed to sit overnight to allow the bacteria to convert all of the nitrate into N_2O gas. The gas in the vials is then introduced via an autosampler into an IsoPrime continuous flow mass spectrometer. The N_2O is analyzed for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, and these values are used to calculate the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the nitrate in the original sample. The raw data is corrected for instrument drift, size linearity, blank

contribution, and fractionation effects by using repeated analyses of five different standards (international standards USGS-34, USGS-35, and IAEA-N3; internal standards 9707 and WEN-D), a standard containing and a blank (vials with media but no added nitrate). All samples are prepared and analyzed in duplicate on the same day, and then analyzed a third or more times until the precisions were acceptable. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are reported in ‰ relative to the Air and VSMOW standards, respectively.

2.3 Water Isotope Analysis

Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water were measured using laser spectroscopy on a Los Gatos Research DLT-100 Liquid-Water Isotope Analyzer, using a modification of the method described in Lis et al. (2008). This instrument uses near infrared absorption spectroscopy to determine the isotopic composition of water samples. 2mL aliquots of sample were loaded into 2mL glass vials with split-cap septa and placed into the auto-sampler. For each sample, 4 to 6 sequential 1.2 μL aliquots of sample were injected into the instrument through the auto-sampler. Two internal water standards were measured after every 5th sample. The results for the first aliquot were discarded to eliminate any memory effect, the remaining aliquots were examined for additional outliers, and the acceptable aliquots were averaged and corrected for permil scale linearity. Each sample is analyzed in duplicate, on different days, and if the repeats didn't match, the samples are reanalyzed again. Precision of this method based on repeated standard measurements is <0.2 ‰ for $\delta^{18}\text{O}$ and <1.0‰ for $\delta^2\text{H}$.

3. Results and Discussion

3.1. Nitrate Isotopes

Sixteen of the 200 wells could not be analyzed for nitrate isotope composition due to low nitrate concentrations. Of these, 15 wells had nitrate concentrations below the detection limit of 0.05 mg/L NO₃-N, and one well had a concentration of 0.07 mg/L NO₃-N. A wide range of δ¹⁵N-NO₃ and δ¹⁸O-NO₃ values were measured within the wells. δ¹⁵N-NO₃ ranged from +2.5 to +25.9 ‰ and δ¹⁸O-NO₃ ranged from -7.7 to +12.2‰. The Stan/Mer and Tul/Kings wells groups has similar ranges of both δ¹⁵N-NO₃ and δ¹⁸O-NO₃. In both the Stan/Mer and Tul/Kings well groups, a much wider range of δ¹⁵N-NO₃ values was measured in the dairy wells in comparison to the non-dairy wells, and many of the dairy wells had higher δ¹⁵N-NO₃ values in comparison to the non-dairy wells (**Figure 2**). With the exception of only two non-dairy wells (61-DOM = +13.9‰, 110-DOM = +10.8‰), all δ¹⁵N-NO₃ values greater than +10‰ were found in dairy region wells. In the Stan/Mer area, median δ¹⁸O-NO₃ values were very similar between the dairy wells and the non-dairy wells, while in the Tul/Kings area the dairy wells had a lower mean and median δ¹⁸O-NO₃ compared to the non-dairy wells (**Figure 3**).

Table 1: Means, standard deviations, medians, and ranges for nitrate isotope composition of different domestic well groups

	Number of wells	Mean (median) δ ¹⁵ N	Range δ ¹⁵ N	Mean & (median) δ ¹⁸ O	Range δ ¹⁸ O
All wells	200	7.3 ± 3.6 (6.1)	2.5 to 25.9	3.1±3.3 (2.6)	-7.7 to 12.2
Stan/Mer all	100	7.5±3.5 (6.2)	2.6 to 18.4	3.5±3.0 (3.1)	-2.3 to 10.7
Tul/Kings all	100	7.1±3.6 (6.0)	2.5 to 25.9	2.6±3.6 (1.9)	-7.7 to 12.2
Stan/Mer dairy	77	8.2±3.7 (7.2)	2.6 to 18.4	3.8±3.1 (3.4)	-2.3 to 10.7
<i>R² for δ¹⁵N and δ¹⁸O-NO₃ = 0.50</i>					

Stan/Mer non-dairy	23	5.3±1.4 (4.8)	3.0 to 8.6	2.3±2.1 (2.3)	-2.1 to 7.6
Tul/Kings dairy	55	8.0±4.6 (6.0)	2.5 to 25.9	1.3±3.4 (0.5)	-7.7 to 9.1
<i>R² for δ¹⁵N and δ¹⁸O-NO₃ = 0.52</i>					
Tul/Kings non-dairy	45	6.2±2.0 (5.8)	2.8 to 13.1	3.9±3.3 (4.3)	-4.2 to 12.2

All isotope values are reported as permil (‰)

3.1.1. Comparison to Dairy Monitoring Wells

The range of $\delta^{15}\text{N}$ and $\delta^{18}\text{O-NO}_3$ values measured in the domestic wells was similar to the ranges measured in the dairy monitoring wells in first-encountered groundwater, although there were some critical differences. The lower boundaries for $\delta^{15}\text{N-NO}_3$ in both the domestic wells and dairy monitoring wells were very similar (lowest $\delta^{15}\text{N}$ domestic = +2.5‰, lowest $\delta^{15}\text{N}$ monitoring = +2.3‰), while the dairy monitoring wells had a much higher upper boundary for $\delta^{18}\text{O-NO}_3$ and for $\delta^{15}\text{N-NO}_3$ (highest $\delta^{15}\text{N}$ domestic = +25.9‰, highest monitoring = +49.9‰), and had a greater percent of individual well measurements of $\delta^{15}\text{N-NO}_3$ above +10‰ (**Figure 4**). This suggests that the dairy monitoring wells captured more nitrate that was almost exclusively derived from manure, while the domestic wells represented mixture with other sources. When samples fell within the lower range of $\delta^{15}\text{N-NO}_3$ values, some domestic wells extended into higher $\delta^{18}\text{O-NO}_3$ values than most monitoring wells. This suggests a source or process impacting some domestic wells that was not observed in the dairy monitoring well data set. It is likely that these higher $\delta^{18}\text{O-NO}_3$ values observed at low $\delta^{15}\text{N-NO}_3$ values were caused either by in-situ nitrification, or by mixing with synthetic nitrate fertilizer. This is discussed in more detail in the following sections.

3.1.2. Comparison Between Groups of Domestic Wells

The four groups of wells (Stan/Mer Dairy and non-dairy, Tul/Kings dairy and non-dairy) exhibit some distinct differences in nitrate isotope patterns, suggesting that different sources and/or processes have different levels of influence within these groups. Both the Stan/Mer dairy wells and the Tul/Kings dairy wells show positive linear relationships between $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$, while the Stan/Mer non-dairy wells and Tul/Kings non-dairy wells showed a weaker, negative relationship between $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$. Because mixing with manure-derived nitrate and the process of denitrification could both result in the linear relationship, other factors such as nitrate concentration and oxygen levels must also be examined. There is quite a bit of uncertainty associated with interpreting the positive linear correlations between the isotopes because many of the wells are at different and/or unknown screen

depths and do not fall along a connected flow path. The positive linear trends for $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}\text{-NO}_3$ for both the Stan/Mer and Tul/Kings dairy groups had similar slopes (0.5 and 0.6, respectively), which are consistent with the expected slope for denitrification (**Figure 5**). However, the expected negative relationship between $\delta^{15}\text{N}$ and NO_3 concentration for in-situ denitrification was not observed and the relationships only have moderate r^2 values (0.50 and 0.52, respectively), suggesting that the high $\delta^{15}\text{N}$ values were not driven primarily by in-situ denitrification but by the presence of manure-derived (or septic system) nitrate. High $\delta^{15}\text{N}\text{-NO}_3$ values were found across a wide range of dissolved oxygen conditions within the domestic wells, and in-situ denitrification typically occurs only when dissolved oxygen levels drop below about 0.5 mg/L (Hubner 1986). Green et al. (2008) found relatively slow rates of denitrification within a set of wells located near the Merced River, and also observed a lack of correlation between nitrate concentrations and other factors associated with denitrification progress. Green et al. concluded that factors such as loading rates were more important in the study area for controlling nitrate concentrations than denitrification. Within the Stan/Mer dairy region, $\delta^{15}\text{N}\text{-NO}_3$ showed significant positive correlations with most major cations and anions, while the opposite trend would be expected if denitrification was removing nitrate and increasing the $\delta^{15}\text{N}\text{-NO}_3$ values.

$\delta^{15}\text{N}\text{-NO}_3$ was negatively correlated to distance from a dairy (lagoon or corral), which is consistent with high $\delta^{15}\text{N}\text{-NO}_3$ from manure-derived nitrate impacting wells within closer proximity to dairies. In the Stan/Mer domestic wells, the overall Spearman's ρ correlation between $\delta^{15}\text{N}\text{-NO}_3$ and distance was -0.55 ($p < 0.001$). Within the Stan/Mer dairy region wells, the correlation was -0.515 ($p < 0.001$), while within the Stan/Mer non-dairy wells, the relationship was -0.253, but was not statistically significant ($p = 0.24$). A similar pattern was observed in the Tul/Kings, with Tul/Kings dairy wells showing a correlation of -0.55 ($p < 0.001$), and no correlation was observed in the Tul/Kings non-dairy wells. The lack of significant correlation in the non-dairy groups suggests that the influence of manure-derived nitrate is not a linear function of distance, and that distance between a well and dairy is only important within a certain range, which will also be influenced by depth to groundwater and vertical and horizontal rates of groundwater movement.

3.1.3. Evaluation of Manure-Derived Nitrate

Based upon the patterns of nitrate isotopes seen in the dairy monitoring wells (see Task Report "Using Nitrate and Water Isotopes to Evaluate Groundwater Quality Beneath Dairy Farms in California") and the results of a study conducted on nitrate isotope distribution within soils beneath several of the dairies in this study (Esser et al., 2009), it appears that partial denitrification may be occurring in the unsaturated zone beneath dairies, resulting in small increases in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the manure-derived nitrate, but that denitrification within the groundwater is not the dominant control on NO_3 concentrations or isotopic values. Based on the currently available data, it appears that the high $\delta^{15}\text{N}\text{-NO}_3$ values measured in some of the domestic wells most likely primarily reflect mixing with a manure-derived nitrate source.

Across the entire data set and the region/land use well groups, $\delta^{15}\text{N}\text{-NO}_3$ was not significantly correlated to NO_3 concentration (**Figure 6**). This indicates two things: 1) in-situ denitrification is not the

primary control on the range of nitrate isotope values, and 2) manure-derived nitrate is not the primary source of nitrate within any of the well groups, although it is an important source of nitrate to some of the individual wells. The lack of correlation between NO_3 concentrations and isotope values suggests that more than one source and multiple processes are contributing to nitrate concentrations within the groundwater. At the lower nitrate isotope values associated with synthetic fertilizer sources (either nitrified prior to reaching groundwater, or nitrified within the groundwater), nitrate concentrations are highly variable, suggesting different amounts of fertilizer-derived nitrate are reaching different wells. In the dairy well groups, the wide ranges of both NO_3 concentrations and nitrate isotope values indicate both large and small contributions of predominantly fertilizer-derived nitrate, large and small contributions of primarily manure-derived nitrate, and the probability that some wells represent a mix of both manure and fertilizer-derived nitrate. Due to the potential variability in the isotopic signatures of the manure and fertilizer end-members, and various processes which will alter the nitrate concentration and isotopic composition, it is not possible to calculate the relative contributions of manure and fertilizer-derived nitrate in wells with intermediate isotope values, it is only possible to make qualitative determinations of the dominant nitrate source.

3.1.4. Evidence of Nitrification and/or Synthetic Nitrate Fertilizer in Non-dairy Wells

In both the Stan/Mer and Tul/Kings non-dairy wells $\delta^{15}\text{N}$ and $\delta^{18}\text{O}-\text{NO}_3$ were not correlated, suggesting that the nitrate isotope compositions in these well groups are controlled either by a mixing of two or more nitrate sources with different $\delta^{18}\text{O}-\text{NO}_3$ values but similar $\delta^{15}\text{N}-\text{NO}_3$ values, or result from biogeochemical processes which affect the nitrogen and oxygen isotopes separately. Nitrate isotope patterns in both groups of non-dairy wells were quite distinct from the patterns seen in the dairy monitoring wells, suggesting the influence of different sources and/or processes (**Figure 7**). Both denitrification and uptake (by phytoplankton and bacteria in surface waters, by bacteria only in groundwater) result in coupled increases in both $\delta^{15}\text{N}-\text{NO}_3$ and $\delta^{18}\text{O}-\text{NO}_3$ (creating a positive linear relationship) as nitrate is removed. Therefore it appears that the nitrate removal processes of either denitrification and/or uptake are dominant processes controlling nitrate concentrations in groundwater within non-dairy regions. Since nitrification leads to the incorporation of oxygen from dissolved oxygen and the surrounding water into the newly formed nitrate molecule, this process can produce a fairly wide range of $\delta^{18}\text{O}-\text{NO}_3$ compositions if there are variations in the water isotope composition across the sampling area. A statistically significant correlation was found between $\delta^{18}\text{O}-\text{NO}_3$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$ in the Tul/Kings non-dairy well group (Spearman's $\rho = 0.58$, $p < 0.001$), suggesting that in-situ nitrification may significantly contribute to the NO_3 concentrations in some of these wells. However, the measured $\delta^{18}\text{O}-\text{NO}_3$ within the Tul/Kings non-dairy well group showed only a weak linear relationship with the predicted $\delta^{18}\text{O}-\text{NO}_3$ calculated for in-situ nitrification based on measured water isotope values ($R^2 = 0.34$). This is consistent with an interpretation that in-situ nitrification has contributed to the NO_3 within this well group, but is not the only source of nitrate, or it is possible that the nitrate isotope pattern is not significantly impacted by nitrification, but instead reflects mixing between two nitrate sources with high and low $\delta^{18}\text{O}-\text{NO}_3$ values and very similar $\delta^{15}\text{N}-\text{NO}_3$ values. Since water isotope composition is strongly related to geographic location in the Tul/Kings well groups, it is also possible that the

relationship between $\delta^{18}\text{O}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-H}_2\text{O}$ might be related to land use patterns instead of in-situ processes. The range of $\delta^{18}\text{O}\text{-NO}_3$ values seen in the non-dairy wells for both Stan/Mer and Tul/Kings could also reflect mixing with nitrate derived from synthetic nitrate fertilizer. Synthetic nitrate fertilizer will have $\delta^{15}\text{N}\text{-NO}_3$ values within the same range as synthetic fertilizers with other forms of nitrogen (ammonium, urea, etc) because the nitrogen is fixed from atmospheric N_2 with $\delta^{15}\text{N} = 0\text{‰}$. In synthetic nitrate fertilizer, the $\delta^{18}\text{O}\text{-NO}_3$ will be distinctly heavy because of the incorporation of atmospheric O_2 ($\delta^{18}\text{O} = +23.5\text{‰}$) during the manufacturing process. Liquid urea ammonium nitrate fertilizer, containing approximately 25% of the total N as NO_3 , is a potentially important type of fertilizer in the San Joaquin Valley, and other fertilizers containing synthetic nitrate might also be locally important (S. Pettygrove, personal communication). Additional work is required to determine the potential importance of synthetic nitrate fertilizer to this area in order to better understand the possible contributions of source mixing versus in-situ nitrification to the Tul/Kings non-dairy wells.

3.2. Water Isotopes

Samples from all 200 domestic wells were analyzed for water isotopic composition ($\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta^2\text{H}\text{-H}_2\text{O}$). $\delta^{18}\text{O}\text{-H}_2\text{O}$ ranged from -13.7 to -6.7‰, and $\delta^2\text{H}\text{-H}_2\text{O}$ ranged from -102.3 to -44.4‰. There was a large region of overlap in water isotope values between the Stan/Mer and Tul/Kings groups of domestic wells, however, mean water isotope values were slightly heavier for the Stan/Mer group of wells (**Figure 8**). Wells in the southern group extended into lighter water isotope values in comparison to the Stan/Mer group, while some wells in the Stan/Mer group showed heavier water isotope values than any wells measured in the southern group. Many wells in both the Stan/Mer and Tul/Kings regions fell below the Global Meteoric Water Line, indicating the water had been affected by evaporation (**Figure 9**). Both dairy and non-dairy wells in the Stan/Mer region had water isotope values indicating evaporation, while it appears that in the Tul/Kings region non-dairy wells showed greater evidence of evaporation in comparison to the Tul/Kings dairy wells. This apparent trend appears to be related to the geographic distribution of the dairies within the valley, rather than a function of land use. Wells located further to the east are primarily in non-dairy regions, and the more eastern wells have both higher elevations and more evaporated water isotope values.

In the Stan/Mer wells, water isotopic composition did not show a linear trend with elevation, while the Tul/Kings wells showed a positive linear correlation between water isotopic composition (using $\delta^{18}\text{O}\text{-H}_2\text{O}$) and elevation ($R^2 = 0.59$) (**Figure 10**). This trend is the opposite of the negative correlation observed for elevation effects on precipitation in the Sierras (Rose et al., 1996). However, the trend is consistent with measurements made by Singleton et al. (2011) for 151 domestic wells surveyed for the GAMA Tulare County Private Domestic Well Survey where lighter water isotopic values were often observed in wells at lower elevations. Singleton et al. attributed the pattern of lighter water isotope values at lower elevations to the heavy use of Kings River water for irrigation, which transports water with light isotopic values from the Sierra Nevada Mountains to the low elevation agricultural areas.

Table 2. Means, standard deviations, medians, and ranges for water isotope composition of different well groups

Group	# of wells	$\delta^{18}\text{O-H}_2\text{O}$	Range $\delta^{18}\text{O-H}_2\text{O}$	$\delta^2\text{H-H}_2\text{O}$	Range $\delta^2\text{H-H}_2\text{O}$
All Wells	200	-10.6±1.7 (-10.7)	-13.7 to -6.7	-78.8±12.0	-102.3 to -44.4
Stan/Mer	100	-10.2 ±1.3 (-10.5)	-12.1 to -6.7	-75.4±9.7	-89.0 to -44.4
Tul/Kings	100	-11.1± 1.8 (-11.1)	-13.6 to -7.7	-82.3±13.1	-102.3 to -59.9
Stan/Mer dairy	77	-10.2 ±1.3 (-10.5)	-12.0 to -6.7	-75.1±9.9	-89.0 to -44.4
Stan/Mer non-dairy	23	-10.2±1.3 (-10.8)	-12.1 to -7.1	-76.3±9.2	-88.6 to -54.7
Tul/Kings dairy	55	-12.2±-1.3 (-12.7)	-13.7 to -8.1	-90.3±10.6	-102.3 to -60.2
Tul/Kings non-dairy	45	-9.7±1.3 (-9.6)	-12.6 to -7.7	-72.6±8.5 (-73.0)	-93.2 to -59.9

The difference in mean water isotope values between the Tul/Kings dairy wells and the Tul/Kings non-dairy wells appears to be primarily a result of different ground elevation distributions between the two land use groups in the Tul/Kings region. The Tul/Kings dairy wells are mostly located in regions of lower ground elevations in comparison to the non-dairy wells. There is a strong positive correlation (Spearman's $\rho = 0.78$, $p < 0.001$) between $\delta^{18}\text{O-H}_2\text{O}$ and ground elevation for the entire group of Tul/Kings wells, as well as within the individual Tul/Kings land use groups (dairy wells spearman's $\rho = 0.62$; non-dairy spearman's $\rho = 0.50$, both $p < 0.001$). Non-dairy wells at lower elevations generally had

lighter water isotope values, similar to the dairy wells, and the dairy wells located at higher elevations generally have heavier water isotope values, suggesting that the differences in water isotope values between the two Tul/Kings land use groups resulted from the different elevation distributions, and not from conditions related directly to land use type.

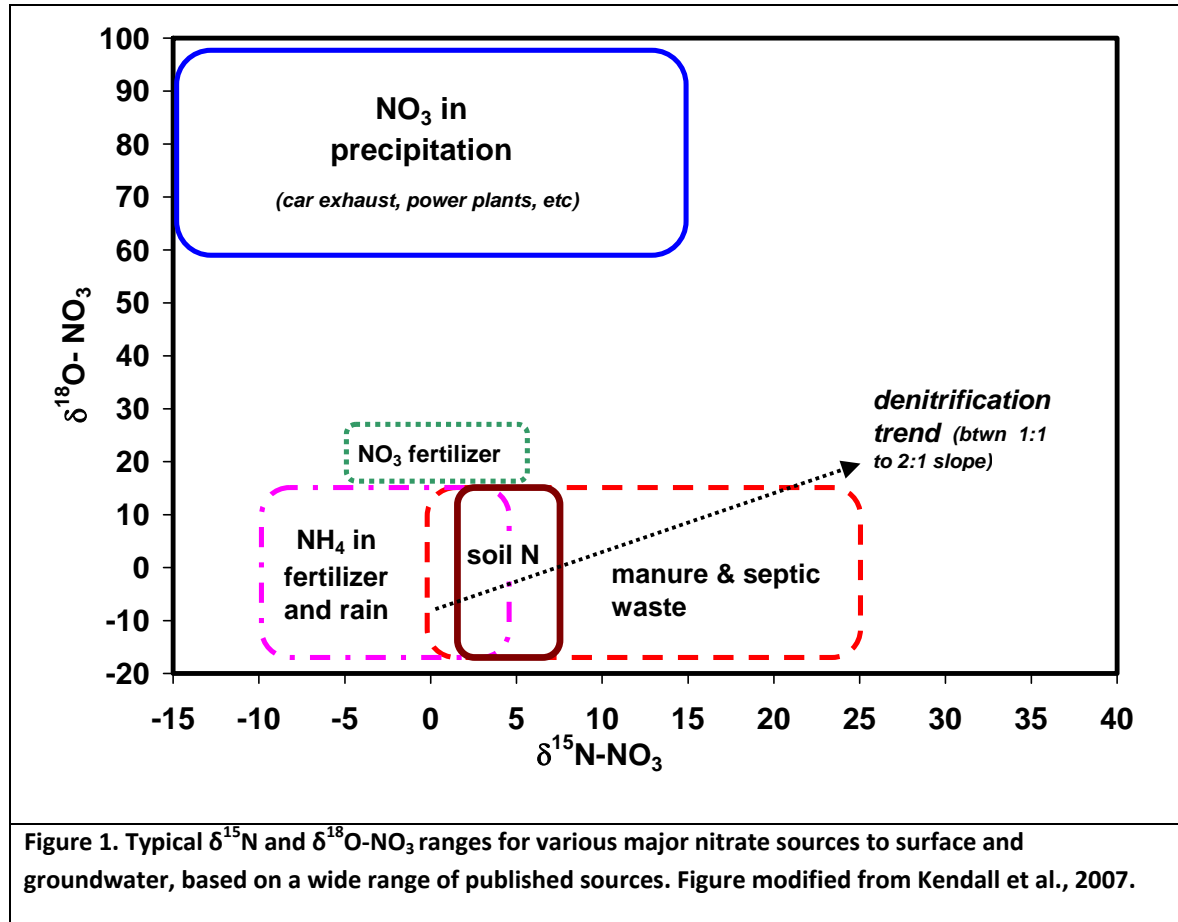
Evaluation of the actual degree of evaporation is difficult because offset of the water isotope values below the Global Meteoric Water Line (GMWL) may result from differences in local precipitation (in arid regions the slope of the Local Meteoric Water Line is often lower than the GMWL slope (Kendall and Coplen 2001), from evaporation during water storage and transport, or from evaporation immediately prior to infiltration. A rough estimate of the relative degree of evaporation can be made by comparing the measured $\delta^2\text{H-H}_2\text{O}$ value of a well sample with the value predicted from GMWL equation using the measured $\delta^{18}\text{O-H}_2\text{O}$ (predicted $\delta^2\text{H-H}_2\text{O} = (8 * \text{measured } \delta^{18}\text{O-H}_2\text{O}) - 10$). The result of this calculation is called the “ $\delta^2\text{H-H}_2\text{O}$ offset” for the purposes of this report. Samples that fall close to or on the GMWL will have more positive $\delta^2\text{H-H}_2\text{O}$ offset values than samples which fall well below the GMWL. Little to no correlation was seen between the calculated $\delta^2\text{H-H}_2\text{O}$ offset and any other measured parameters in the Stan/Mer wells, but wells in the Tul/Kings region showed interesting patterns which may be useful in understanding water use. In the entire Tul/Kings data set, $\delta^2\text{H-H}_2\text{O}$ offset was moderately and statistically significant negatively correlated to concentrations of most of the major cations and anions, including nitrate. This indicates that water which may have undergone more evaporation is associated with higher concentrations of cations and anions. Agricultural practices including transportation of water in open canals, storage, and irrigation can lead to greater amounts of evaporation, and it appears that this water tends to carry higher concentrations of solutes in comparison to water that has undergone less apparent evaporation. Offset below the GMWL therefore appears to be an indicator of greater potential water quality impacts in the Tul/Kings region.

4. Summary of Findings and Conclusions

- $\delta^{15}\text{N-NO}_3$ values above +10‰ (consistent with manure-derived nitrate) were found almost exclusively in Stan/Mer and Tul/Kings wells that were within 2.4 km of a dairy lagoon or corral.
- Within the Dairy well groups in Stan/Mer and Tul/Kings, $\delta^{15}\text{N-NO}_3$ was significantly negatively correlated to distance from a dairy corral or waste lagoon, consistent with the interpretation that the higher $\delta^{15}\text{N-NO}_3$ values reflect greater contributions of manure-derived nitrate. In both non-dairy groups, $\delta^{15}\text{N-NO}_3$ was not correlated to distance from dairy, suggesting that there is a distance threshold past which the influence of manure-derived nitrate can no longer be detected.
- In comparison to the dairy monitoring wells which sample from near the top of the water table, the domestic wells in the dairy groups showed similar trends of nitrate isotope compositions, but had both lower median $\delta^{15}\text{N-NO}_3$ values and lower median NO_3 concentrations, indicating that although some of the domestic wells have been impacted by manure-derived nitrate, the impacts were lower than what was seen at or near the water table beneath the dairies.
- $\delta^{15}\text{N-NO}_3$ values were not correlated to NO_3 concentrations, and a wide range of NO_3 concentrations was found across wells. The spread of both NO_3 concentrations and isotope compositions indicates that high NO_3 in the study area can be dominated by fertilizer-derived nitrate, manure-derived nitrate, or a mixture of the two sources, depending upon the individual well.
- The relationships between $\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$, NO_3 concentration, and dissolved oxygen in the Stan/Mer and Tul/Kings suggest that partial denitrification, most likely within the unsaturated zone or top of the water table, contributes to higher nitrate isotope values, the occurrence of high $\delta^{15}\text{N-NO}_3$ values measured in a portion of the domestic wells is driven primarily by a manure-derived isotopic signal.
- In both the Stan/Mer and Tul/Kings non-dairy domestic well groups, the relationship between $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ was very different from the one seen in the dairy domestic well groups and in the dairy monitoring wells, and a wide range of $\delta^{18}\text{O-NO}_3$ values was measured within a fairly narrow and low range of $\delta^{15}\text{N-NO}_3$ values. This suggests that the sources and processes controlling NO_3 concentration distributions in the non-dairy groups are distinct from what was observed near the top of the water table directly beneath dairies. The most likely factors controlling the nitrate isotope composition of NO_3 concentrations in the non-dairy domestic well groups appear to be either nitrification and/or mixing with synthetic NO_3 fertilizer. The significant correlation between $\delta^{18}\text{O-NO}_3$ and $\delta^{18}\text{O-H}_2\text{O}$ in the Tul/Kings non-dairy wells suggests the influence of in-situ nitrification on the NO_3 concentrations in these wells.

- Water isotopic composition in the Tul/Kings area was positively correlated to elevation, reflecting the transportation of water derived from higher elevations into the valley for irrigation purposes. No correlation was found between water isotope composition and elevation in the Stan/Mer area.
- In the Tul/Kings region, water that appeared to have a more evaporated signal (fell more below the Global Meteoric Water Line) was correlated to higher concentrations of most of the major cations and anions. This may be related to evaporation occurring during agricultural activities which also transport solutes to the groundwater, the more evaporated water may originally carry higher solute concentrations which then travel to the groundwater, or the transportation to and use of water with a more evaporated signal may occur primarily in areas where land use activities result in higher solute loading in the groundwater.

5. Figures



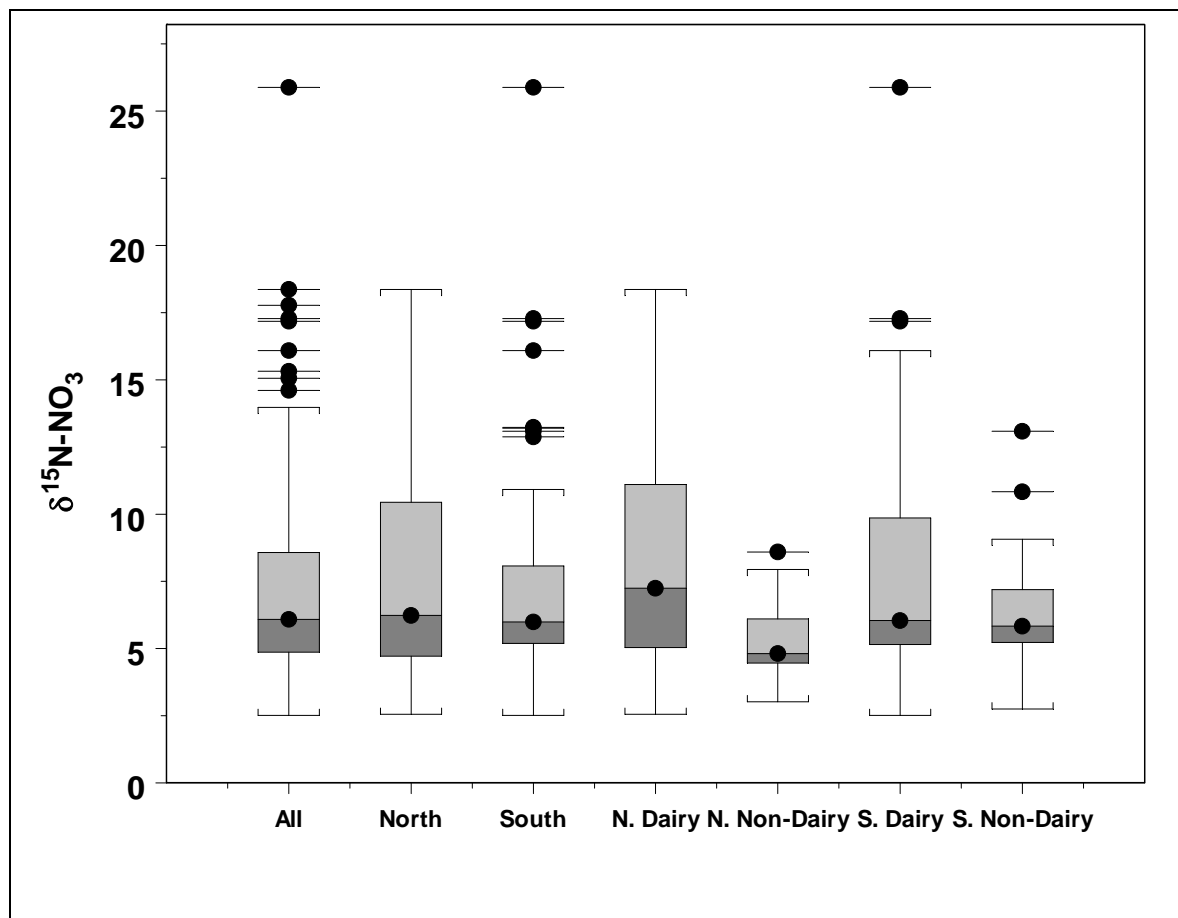
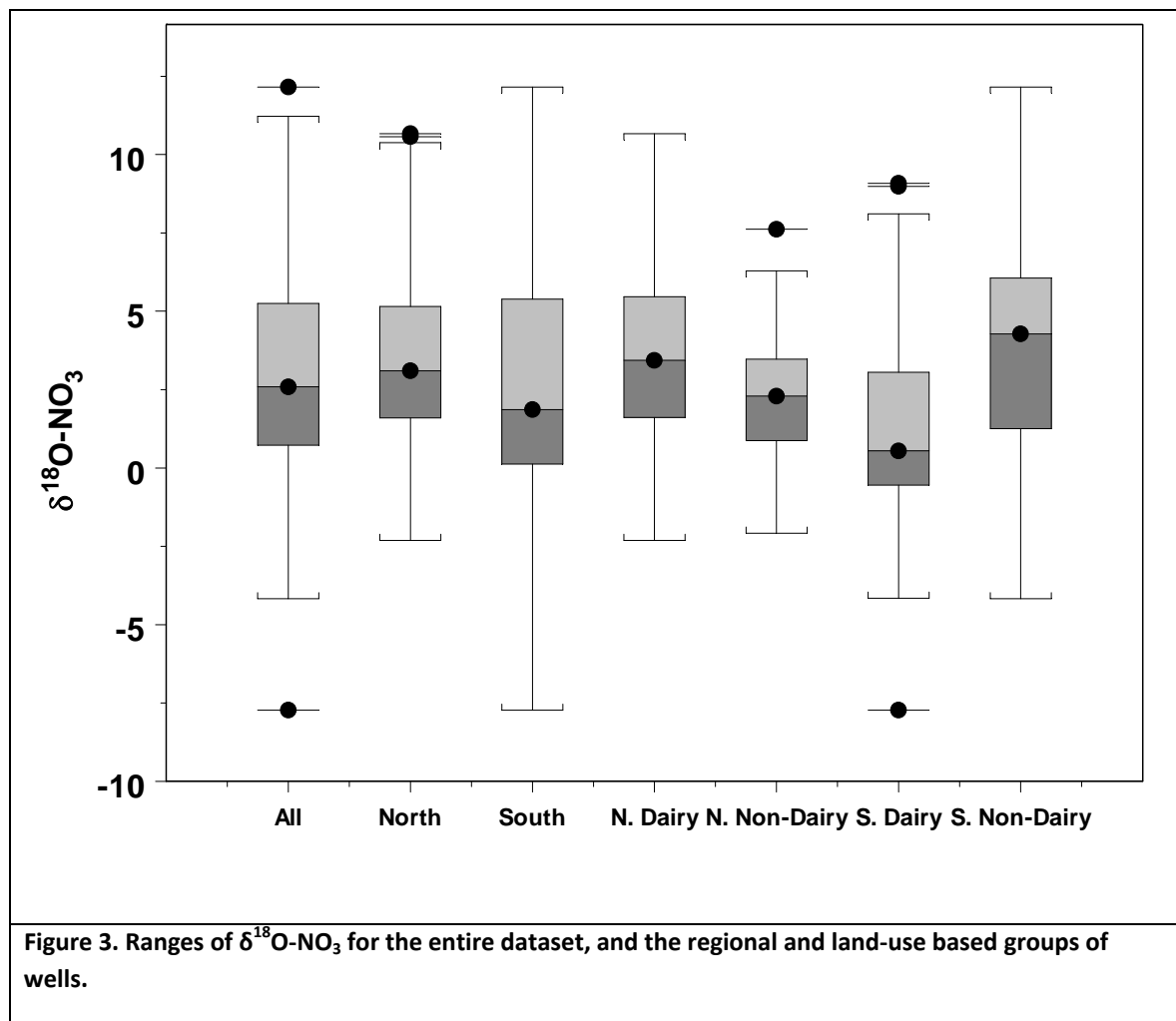


Figure 2. Ranges of $\delta^{15}\text{N-NO}_3$ for the entire dataset, and the regional and land-use based groups of wells. Note the narrower ranges for the non-dairy groups, and the greater percentages of samples in the dairy groups extending into the higher $\delta^{15}\text{N-NO}_3$ values.



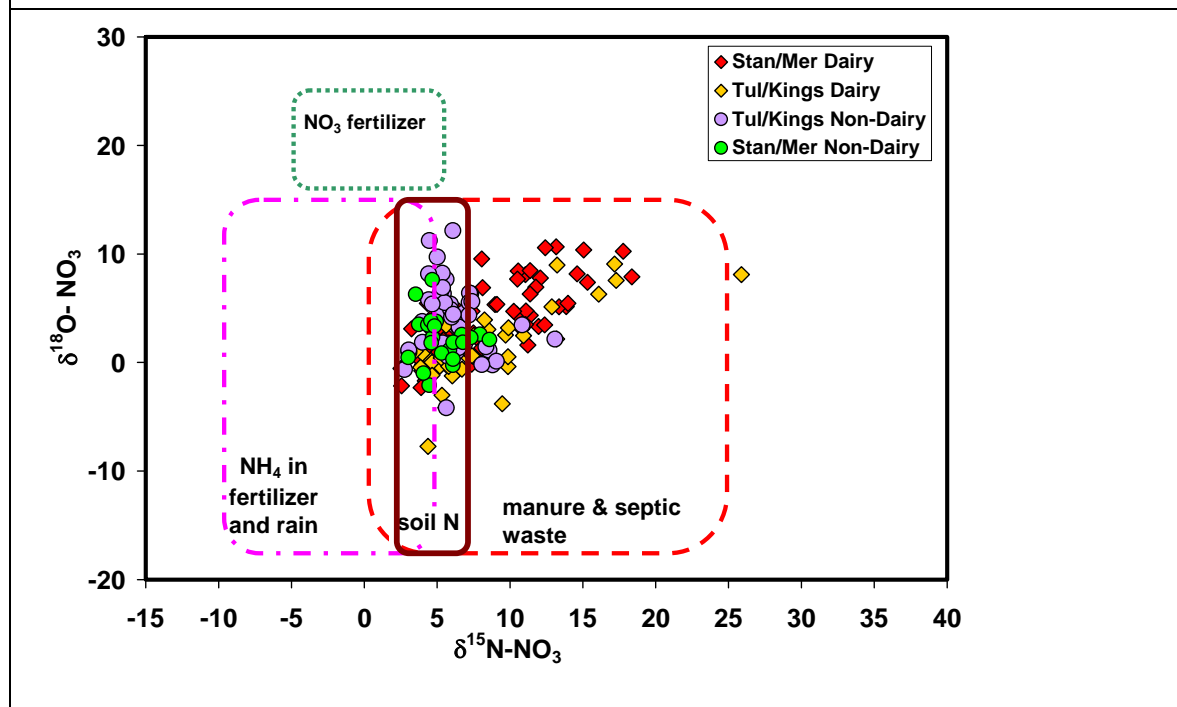
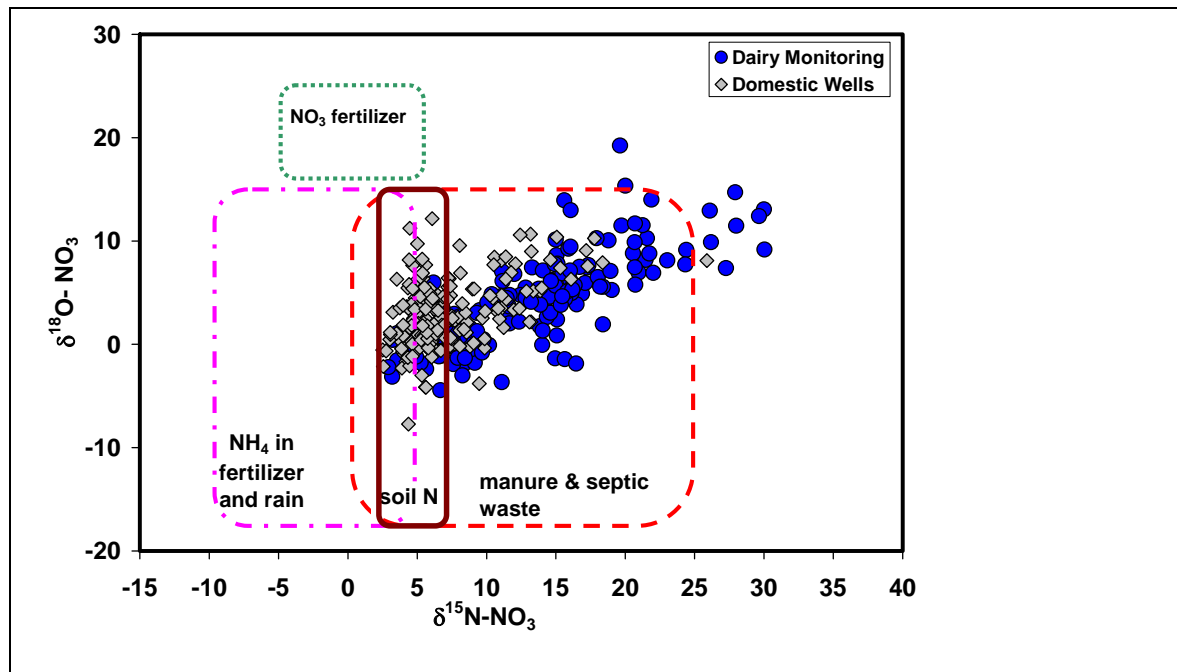


Figure 4a & b. Comparison plot of nitrate isotope distributions for the domestic wells and the dairy monitoring wells (a), and for the different groups of domestic wells (b). The dairy monitoring well group has more individual wells extending into higher $\delta^{15}\text{N-NO}_3$ values, while the domestic well group shows a greater range of $\delta^{18}\text{O-NO}_3$ values occurring in the lower range of $\delta^{15}\text{N-NO}_3$. The dairy monitoring well with the highest $\delta^{15}\text{N-NO}_3$ values (+41.1‰ to +49.4‰) has been left off the graph. Boxes based on Kendall et al., 2007.

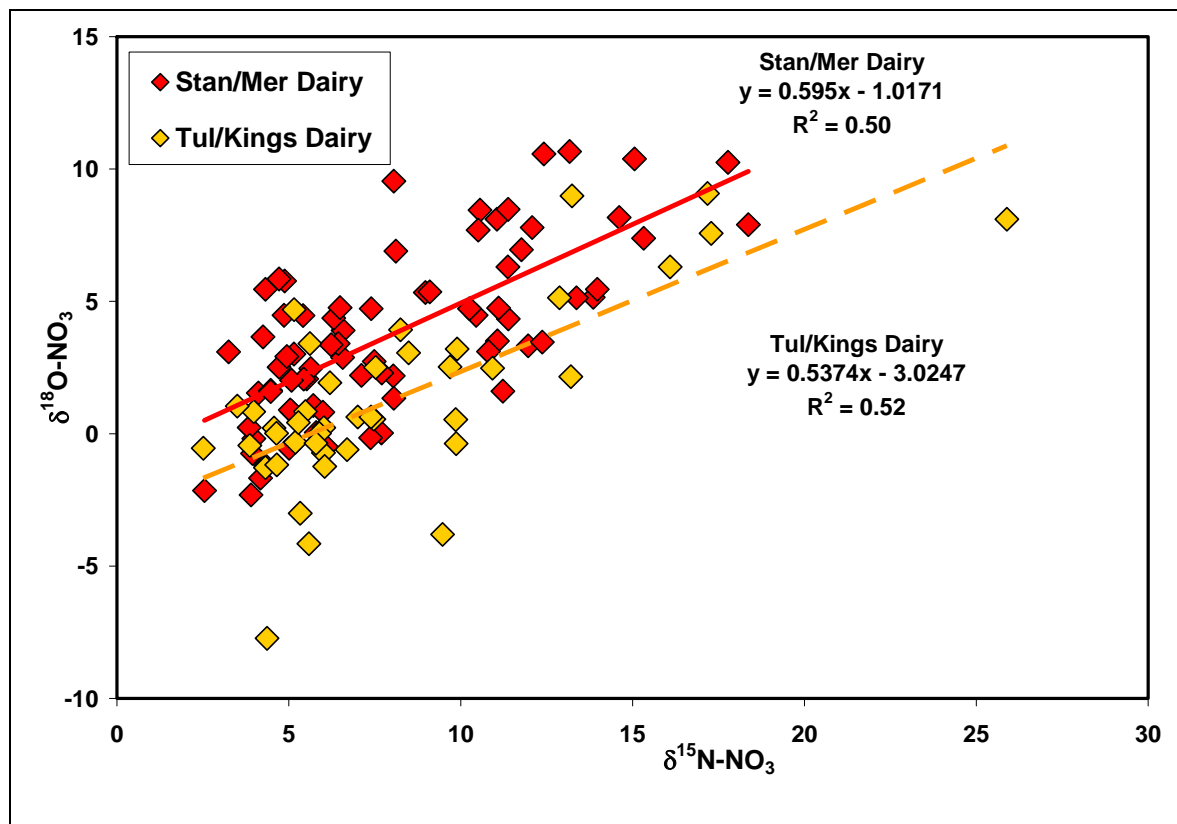


Figure 5. Linear relationships between $\delta^{15}\text{N}$ and $\delta^{18}\text{O-NO}_3$ for the two groups of Dairy region wells. The slopes are similar and consistent with denitrification, but are also consistent with mixing with a manure-derived nitrate source.

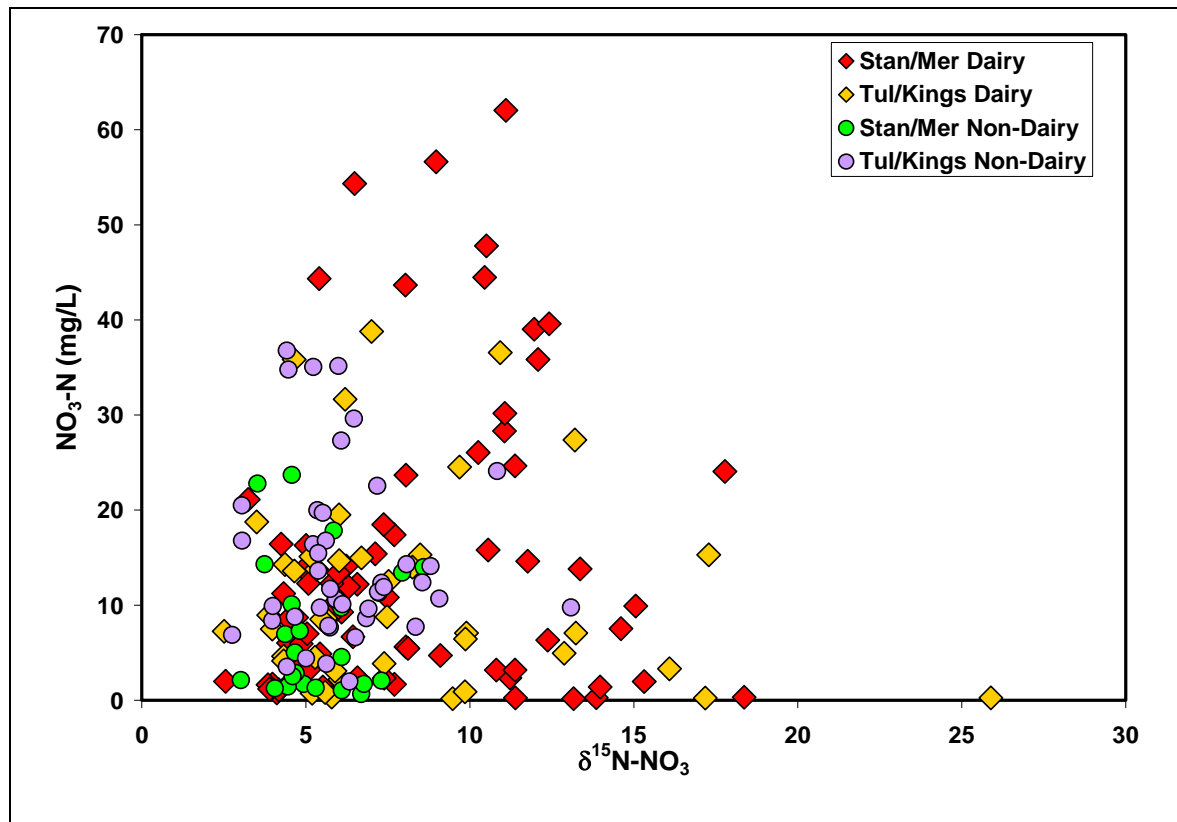


Figure 6. Comparison of $\delta^{15}\text{N-NO}_3$ and NO₃ concentration for the four groups of domestic wells. High NO₃ concentrations occur across a wide range of $\delta^{15}\text{N-NO}_3$ values, indicating that greater NO₃ impacts are not associated with a single source of NO₃.

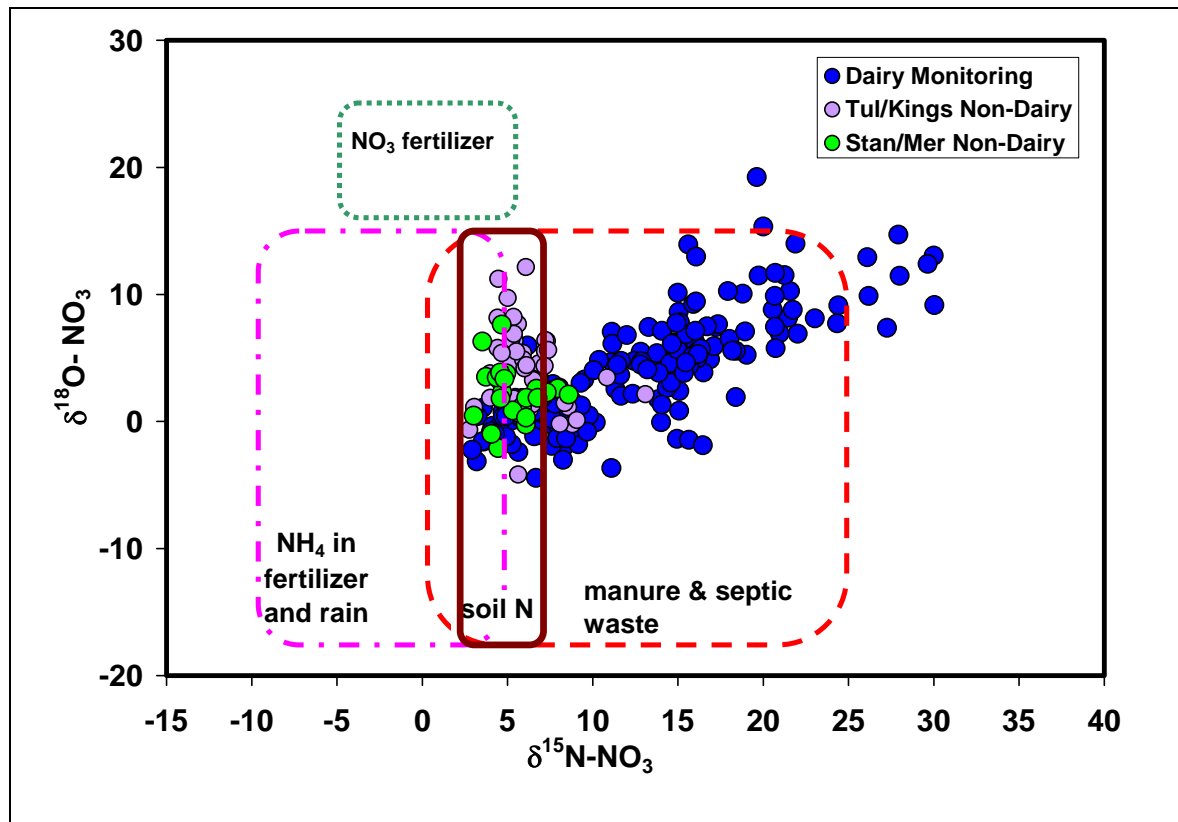
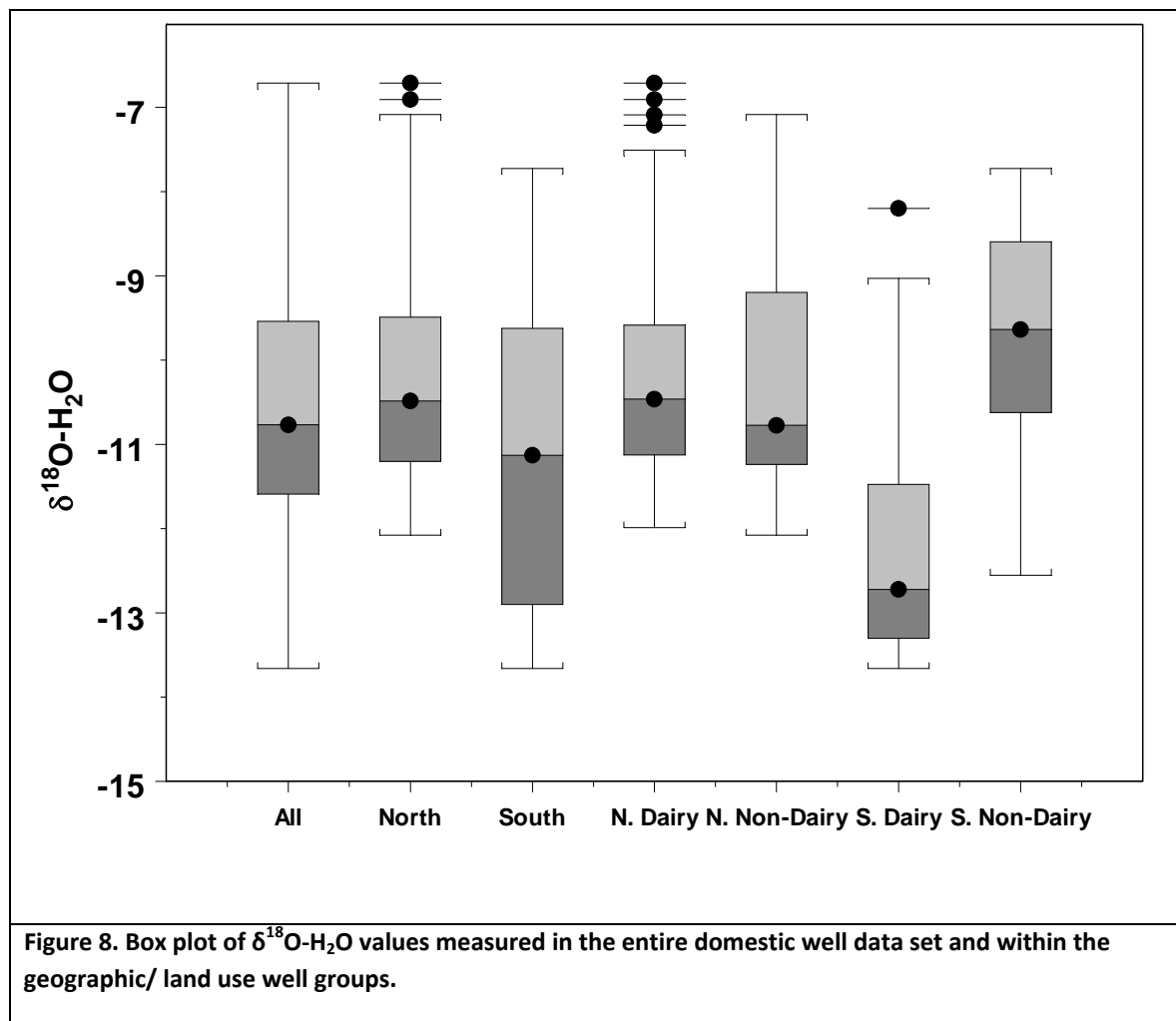


Figure 7. Nitrate isotope distributions in the Stan/Mer and Tul/Kings non-dairy wells in comparison to data from the dairy monitoring wells. Note the distinct difference in the relationship between $\delta^{15}\text{N}-\text{NO}_3$ and $\delta^{18}\text{O}-\text{NO}_3$ for the dairy monitoring wells in comparison to the non-dairy domestic well groups.



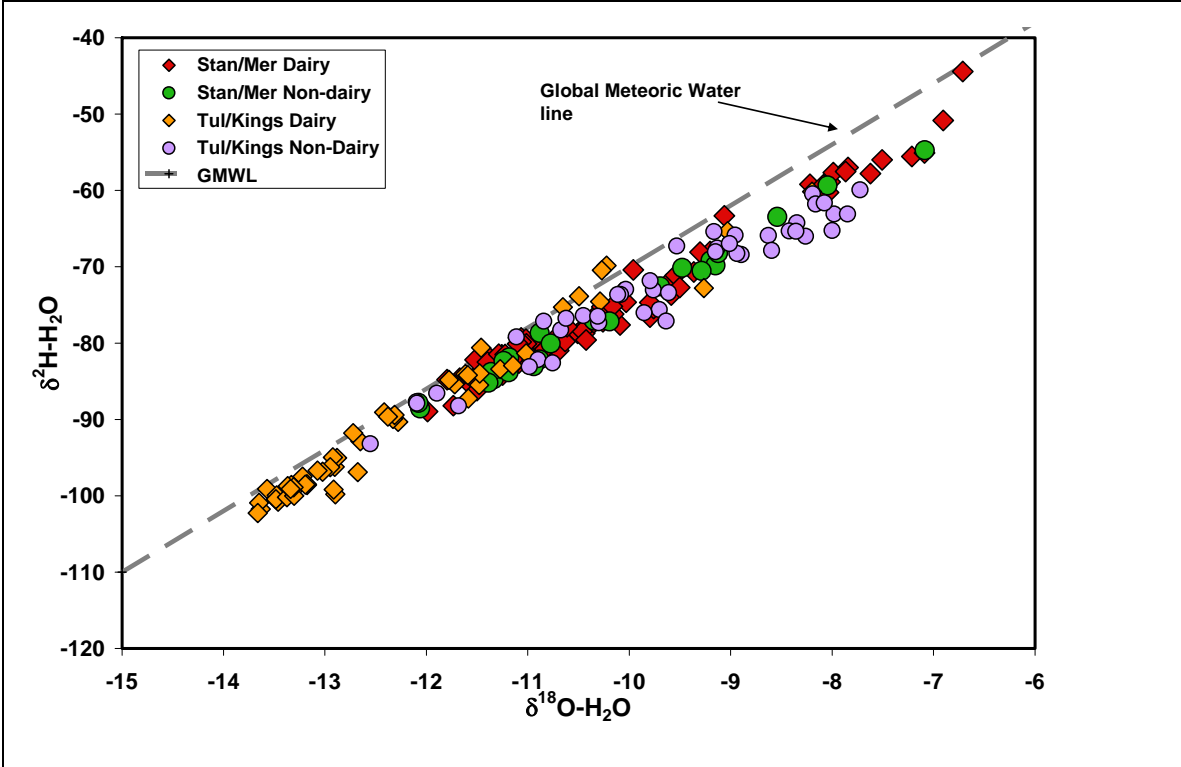


Figure 9. Water isotope composition of all domestic well samples from the domestic wells.

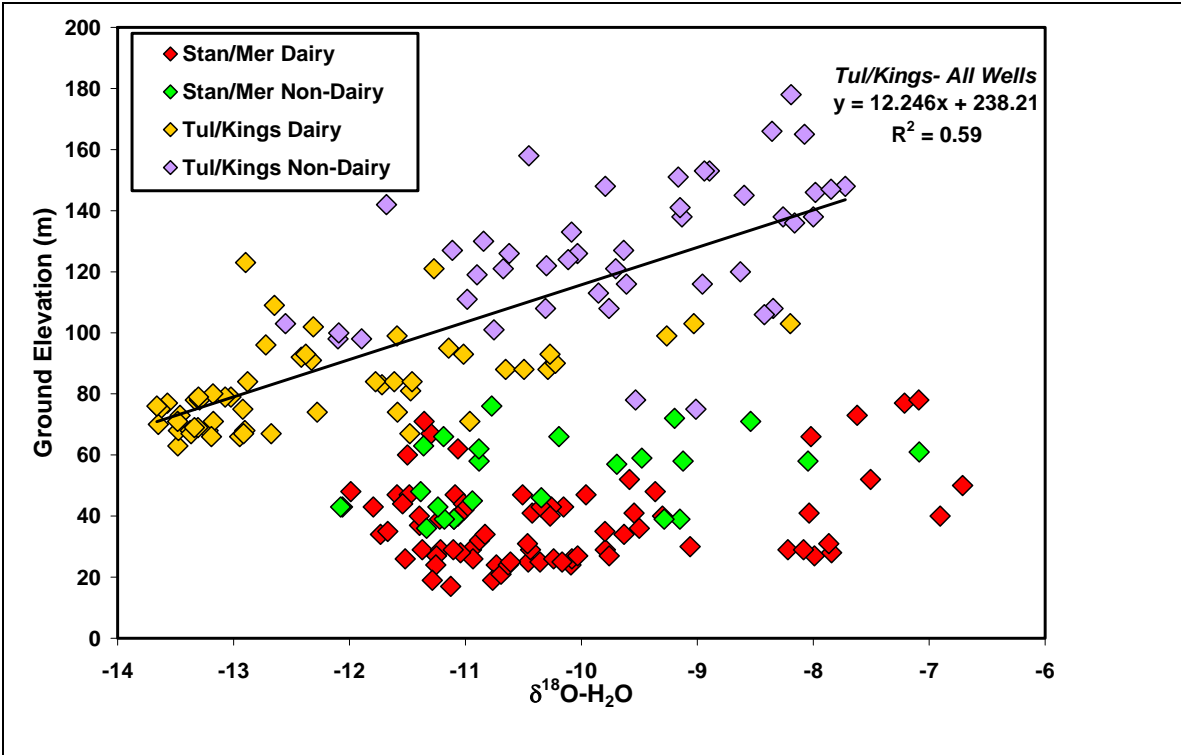


Figure 10. Domestic wells in the Tul/Kings study area showed higher water isotope values with increasing elevation, the opposite of the observed elevation effect in precipitation. The lower values at the low elevation sites reflect the use of imported irrigation water (Singleton et al., 2011).

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